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(54) **Photocurable compositions**

(57) Photocurable compositions include a photopolymerisable binder comprising a water reducible multi-functional polyurethane acrylate oligomer, a multi-functional acrylate monomer, water, and a vinyl ether monomer, and a free radical photoinitiator. They show properties exhibited by similar compositions containing N-vinyl-2-pyrrolidone without containing it, and can be used to produce prints on paper and paper related products without the release of harmful solvents or monomers.

The composition may be in the form of a varnish or lacquer, or may include a colorant and be in the form of an ink, e.g. for screen printing.

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#### PHOTOCURABLE COMPOSITIONS

This invention concerns photocurable compositions, for example for producing prints and printed display graphics on paper and paper related products, e.g. card and corrugated card.

Examples of hitherto proposed compositions for such end uses include:-

(i) Cellulosic polymers and a co-resin, e.g. a rosin modified phenolic dispersed in an aromatic hydrocarbon solvent, flow control agents and colorants being present. Compositions of this type typically have a solids content of 35 to 50 percent by weight and they dry by evaporation of the solvent.

(ii) Alkali susceptible acrylic resins dispersed in water with a coalescing agent, neutralizing agents and flow agents. Drying is effected by the action of heat evaporating the water and causing the composition to coalesce. The solids content of these compositions is typically 25 to 60 percent by weight.

(iii) Epoxy acrylate polymers and/or polyurethane acrylate oligomers dispersed in mono- and/or multi-functional acrylate monomers with a free radical initiator. Again, flow agents and colorants would be present. Curing is effected by exposure of the compositions to ultraviolet light. The curable materials represent 100 percent of these compositions.

Coatings of compositions of type (i) in the form of inks can be dried quickly and give good color depth and cleanliness of tone. However, the solvent in the compositions can cause press stability problems as a result of solvent evaporation from the ink on the printing press. Furthermore, the solvent which must be evaporated to effect full drying can pose environmental problems.

Compositions of type (ii), although potentially environmentally safer than compositions of type (i), can give rise to problems in use, the high water content (25 to 60 percent), leading to the substrate to which they are applied being affected causing curling and cockle. When producing multiple prints by repeated printing on the same substrate over previous printing, rewetting of the earlier prints takes place, which can be disadvantageous.

Coatings of compositions of type (iii) can be cured very rapidly, but the cured coatings tend to be very glossy with a high build due to the 100 percent content of polymerizables. This can be a particular problem when multiple printing is effected, leading to the print having poor 'feel'.

More recently it has been proposed to combine the high speed curing which can be effected with free radically curable compositions with the greater environmental safety of water-containing compositions, to achieve free radically curable compositions which can be reduced in viscosity by the addition of water. Water in the compositions is removed

during the ultra-violet curing operation, leading to rapidly curable coatings which have a low feel, due to the lower overall solids content of about 65 percent, without the problems encountered with compositions of type (ii). A typical composition of this type would consist of a water-tolerant epoxy acrylate and/or a polyurethane acrylate dispersed in multi-functional acrylate monomers with a free radical initiator, water being present in an amount of from 25 to 40 percent by weight of the composition. Flow agents and colorants would also be present.

Compositions of this type generally benefit from the addition of a vinyl-pyrrolidone derivative, e.g. N-vinyl-2-pyrrolidone, these derivatives having an excellent viscosity reducing action, only small quantities being required to achieve a high degree of viscosity reduction. This is unlike the effect of other acrylate monomers or indeed water.

More recently, compositions containing vinyl-pyrrolidone derivatives have come under scrutiny on health and safety grounds, and their use in commercial compositions, for example in the screen printing industry, is becoming less desirable.

Although mono-functional and/or multi-functional acrylate monomers may be used in place of N-vinyl-2-pyrrolidone, the viscosity reducing action of most is inferior to that of N-vinyl-2-pyrrolidone.

It has been proposed to use vinyl ethers in ultra-violet initiated, cationically curable compositions, these ethers having some properties in common with N-vinyl-2-pyrrolidone, e.g. viscosity reduction, although they are thought not to take part readily in free radical initiated reactions.

According to the present invention there is provided a photocurable composition comprising:-

photocurable composition comprising:-

- (a) a photopolymerisable binder comprising a water reducible multi-functional polyurethane acrylate oligomer, a multi-functional acrylate monomer, water, and a vinyl ether monomer; and
- (b) a free radical photoinitiator.

Surprisingly, compositions of the present invention have exhibited similar desirable properties to those containing N-vinyl-2- pyrrolidone but without containing it.

The multi-, e.g. di- or tri-, functional polyurethane acrylate oligomers should be water reducible, i.e. be dilutable with water. They are preferably liquid or semi-solid at ambient temperature. They can be formed by known methods, for example by reacting an aromatic isocyanate, e.g. toluene di-isocyanate, with 2-hydroxyethyl acrylate. Prior to acrylation of the isocyanate, it can, if desired, be extended to modify the properties of the oligomer obtained after acrylation. Compositions of the present invention preferably contain from 20 to 60 percent by weight of a multi-functional polyurethane acrylate oligomer.

The multi-, e.g. di-, tri- or tetra-, functional acrylate monomer usually serves to increase the crosslink density of the compositions, and thus impart a harder cured film surface. Examples of such monomers include alkyleneoxy diacrylates, e.g. triethylene glycol diacrylate, tripropylene glycol diacrylate; propoxylated neo-pentyl glycol diacrylate; and acrylates of triols and alkoxy extended triols, e.g. trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate and propoxylated trimethylolpropane triacrylate. The multi-functional acrylate monomer is preferably present in an amount of from 8 to 35 percent by weight of the composition.

The vinyl ether is preferably present in an amount of from 2 to 30 percent by weight based on the composition. Typically the vinyl ether will have a boiling point of from 100 to 200°C. Examples of vinyl ethers which can be used include 1,4-cyclohexane dimethanol divinyl ether, hydroxybutyl vinyl ether, triethylene glycol divinyl ether, hydroxybutyl vinyl ether iso-phthalate and 1,4-cyclohexane dimethanol divinyl ether glutarate ester.

The photoinitiator should be capable of producing free radicals upon irradiation by ultra-violet light. Any of a wide variety of photoinitiators can be used, mixtures of liquid aryl ketones being preferred. The amount of photoinitiator used will usually be from 2 to 10 percent based on the total photopolymerisable materials in the compositions. Some latitude is generally allowed to compensate for pigment blocking effects.

Water preferably represents from 10 to 50 percent by weight of compositions of the present invention. It can be common tap water, but it is more preferably deionised water, calcium ions for example having been replaced by hydrogen ions or a solubilising metal ion by a single passage of tap water over an ion-exchange resin, e.g. Amberlite (Trade Mark). However, the degree of hardness of the water has not been found to be a critical factor.

Compositions of the present invention can be in the form of a photocurable varnish or lacquer. However, they preferably include a colorant, for example a pigment, either as a dry powder or as a pigment dispersion, and a surfactant. When used as a dispersion, e.g. in ethylene glycol, the pigment preferably represents about 50 percent of the dispersion. When present as a dry pigment the colorant preferably forms from 1 to 30 percent by weight of the compositions. Pigmented compositions of the present invention are

advantageously in the form of inks, for example for screen printing.

Other materials which can be present in compositions of the present invention include flow controllers, for example polyacrylates (e.g. Modaflow - ex Monsanto); silicone fluids, for example as 100 percent solutions of poly-(methyl siloxanes) (e.g. Fl111/100); and materials known for modifying the surface properties of such compositions, for example polyethylene or polypropylene waxes (e.g. Polymist B-6 - ex Allied Chemicals), typically in the amounts used hitherto.

Compositions of the present invention will generally be used and cured by applying them to a substrate and thereafter exposing them to a source of ultra-violet radiation to cure and harden them.

The present invention therefore further provides a method of producing a cured coating on a substrate, the method comprising applying a composition according to the invention to a substrate and thereafter exposing the composition to ultra-violet light to effect free radical curing of the composition. The substrate can be of paper, card or a corrugated/fluted card.

Compositions of the present invention have been of particular value in forming screen printed decorations on flat paper/cardboard substrates for graphic arts and display, without the release of harmful solvents or monomers, whilst retaining desirable properties normally associated with formulations containing N-vinyl-2-pyrrolidone or a solvent.

The following Examples are given by way of illustration only. All parts are percentages by weight of the total composition unless stated otherwise. A tri-functional water reducible polyurethane acrylate used in each of the Examples.

### Example 1

An ink was prepared by mixing the following ingredients, followed by roll grinding:-

water reducible polyurethane acrylate oligomer	35 parts
water	35 parts
ethoxylated trimethylol propane triacrylate	8 parts
photoinitiator	5 parts
1,4-cyclohectane dimethanol-divinyl ether	8 parts
levelling agent (Fl11/100)	2 parts
wax (Polymist Bl2)	0.5 part
pigment (e.g. Pigment Red 2)	6.5 parts

This ink was printed by screen printing techniques on to a medium weight art paper using a polyurethane squeegee and a semi-automatic Svecia flat bed printer with a 150 mesh screen. The print so produced was cured by exposure to  $150 \text{ mJ/cm}^2$  of ultra-violet light from a pair of 80W/cm medium pressure mercury vapor lamps having a spectral output predominantly at a wavelength of 284 and 365 nm. The cured print was assessed for water resistance, gloss, curl, rub/scuff and feel.

The results of these tests are given in the accompanying Table.

### Example 2

An ink was prepared as described in Example 1 by mixing and roll grinding the following ingredients:-

water reducible polyurethane acrylate oligomer	35 parts
water	35 parts
ethoxylated trimethylol propane triacrylate	8 parts
photoinitiator	5 parts
tripropylene glycol divinyl ether	8 parts



levelling agent (Fl111/100)	2 parts
wax (Polymist Bl2)	0.5 part
pigment (e.g. Pigment Red 2)	6.5 parts

This ink was printed and tested as described in Example 1, the results being given in the accompanying Table.

### Example 3

An ink was prepared as described in Example 1 by mixing and roll grinding the following ingredients:-

water reducible polyurethane acrylate	35 parts
water	35 parts
ethoxylated trimethylol propane triacrylate	8 parts
photoinitiator	5 parts
hydroxybutyl vinyl ether	8 parts
levelling agent (Fl111/100)	2 parts
wax (Polymist Bl2)	0.5 part
pigment (e.g. Pigment Red 2)	6.5 parts

This ink was printed and tested as described in Example 1, the results being given in the accompanying Table.

### Example 4 (comparison)

An ink was prepared as described in Example 1 by mixing and roll grinding the following ingredients:-

water reducible polyurethane acrylate	35 parts
water	35 parts
ethoxylated trimethylol propane triacrylate	8 parts
photoinitiator	5 parts
N-vinyl-2-pyrrolidone	8 parts
levelling agent (Fl111/100)	2 parts
wax (Polymist Bl2)	0.5 part
pigment (e.g. Pigment Red 2)	6.5 parts

This ink was printed and tested as described in Example 1, the results being given in the accompanying Table.

Table

Example	Water resistance	Gloss	Curl	Rub/Scuff	Feel
1	4	5	4	5	5
2	5	4	4	5	5
3	5	5	5	5	4
4	5	5	4	5	5

The compositions of Examples 1, 2 and 3 were substantially equivalent to or indeed even superior to that of Example 4 which contained N-vinyl-2-pyrrolidone.

Claims

1. A photocurable composition comprising:-
  - (a) a photopolymerisable binder comprising a water reducible multi-functional polyurethane acrylate oligomer, a multi-functional acrylate monomer, water, and a vinyl ether monomer; and
  - (b) a free radical photoinitiator.
2. A composition according to claim 1, wherein the photopolymerisable binder represents from 20 to 60 percent by weight of the composition.
3. A composition according to claim 1 or claim 2, wherein the water is tap water or deionised water.
4. A composition according to any of the preceding claims, wherein the water represents from 10 to 50 percent by weight of the composition.
5. A composition according to any of the preceding claims, wherein the vinyl ether has a boiling point of from 110 to 200°C.
6. A composition according to any of the preceding claims, wherein the vinyl ether represents from 2 to 30 percent by weight of the composition.
7. A composition according to any of the preceding claims, including a colorant.
8. A composition according to claim 7, wherein the colorant represents from 1 to 30 percent by weight of the composition.

9. A composition according to any of the preceding claims, in the form of an ink.

10. A method of producing a cured coating on a substrate, the method comprising applying a composition according to any of the preceding claims to a substrate and thereafter exposing the composition to ultra-violet light to effect free radical curing of the composition.

11. A method according to claim 10, wherein the substrate comprises paper, card or a corrugated/fluted card.

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Relevant Technical fields

(i) UK CI (Edition K ) C3V (VBC, VABD, VABE, VAD, VABP)  
 C3P (PDIE, PDIC, PEB, PFE)  
 (ii) Int CL (Edition 5 ) C08F; C09D

Search Examiner

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Databases (see over)

(i) UK Patent Office

(ii) ON-LINE DATABASES: - WPI

Date of Search

3 JULY 1992

Documents considered relevant following a search in respect of claims

1 TO 11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	EP 0155704 A2 (UNION CARBIDE) See Claims 1, 9, Examples 1 to 3, page 38 lines 19-26, page 39 lines 23, 24	1, 7, 10, 11
A	EP 0077074 A1 (DE SOTO) See claims, Examples page 4 lines 8, 9	1, 10

Category	Identity of document and relevant passages	Relevant to claim(s)

#### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

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